

# CLAY MINERALOGY AND CRYSTALLINITY AS A CLIMATIC INDICATOR: EVIDENCE FOR BOTH COLD AND TEMPERATE CONDITIONS ON EARLY MARS.

B. Horgan<sup>1</sup>, A. Rutledge<sup>2</sup>, and E. B. Rampe<sup>3</sup>,  
<sup>1</sup>Dept. of Earth, Atmospheric, and Planetary Sciences, Purdue University (briony@purdue.edu), <sup>2</sup>School of Earth and Space Exploration, Arizona State University, <sup>3</sup>Aerodyne - Jacobs JETS contract NASA Johnson Space Center.

**Introduction:** Surface weathering on Earth is driven by precipitation (rain/snow melt). Here we summarize the influence of climate on minerals produced during surface weathering, based on terrestrial literature and our new laboratory analyses of weathering products from glacial analog sites. By comparison to minerals identified in likely surface environments on Mars, we evaluate the implications for early martian climate.

**Main points:** (1) Warm, arid climates cause surface weathering due to rain, and mainly produce well-crystalline smectite clays, similar to those found on Mars at Mawrth Vallis and in widespread clay leaching profiles. (2) Cold climates cause weathering due to snow/ice melt, and mainly produce poorly crystalline minerals, similar to those found *in situ* at Gale and Gusev Craters. (3) In any climate, sustained weathering produces highly leached kaolin clays, as observed at the top of the widespread leaching profiles on Mars. Together, these observations suggest that Mars experienced both sustained cold climates and one or more sustained eras of at least seasonally temperate climates.

**Weathering in warm climates:** In climates where aqueous surface weathering is driven primarily by rainfall at low to modest precipitation rates (approximately <1 meter mean annual precipitation), weathering preferentially leaches mobile cations (*e.g.*, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup>). These are then incorporated into smectites of similar composition to their host sediments, often forming thick clay-rich (up to 95 wt.%) subsurface horizons. At somewhat higher precipitation rates, or if arid soils are weathered for sustained periods (100k-1M years), mobile cations are removed from the system entirely and kaolin clays are formed [1,2]. Long-term arid weathering is one hypothesis for the origin of widespread laterites in the Australian Outback [3].

**Warm climates on early Mars?** On Mars, thick (>100m) stacks of smectite-bearing layers at sites like Mawrth Vallis are consistent with soil sequences [4]. Furthermore, thin (<5m) stacks of Al-clays overlying Fe/Mg-smectites have been identified in diverse ancient settings across Mars, and are consistent with laterite-like leaching profiles [5]. These observations suggest at least one era of sustained temperate and arid or wetter climate during the late Noachian.

**Weathering in cold climates:** Very high leaching rates tend to favor the rapid precipitation of poorly-crystalline phases, like the aluminosilicate allophane [6]. High leaching rates occur due to overall high pre-

cipitation rates (*e.g.*, a few meters MAP), seasonal monsoons in an otherwise arid climate (the deserts of Hawaii), or weathering of glass in tephra (Iceland) [7]. However, high leaching rates are also caused by the rapid onset of seasonal melting in cold environments, where precipitation mainly falls as snow. Thus, alpine soils are commonly dominated by poorly crystalline phases, which then mature into kaolin minerals [8].

## Laboratory analysis of pro-glacial weathering:

To test our hypothesis that sub-aerial weathering by snow/ice melt produces mainly poorly crystalline phases, sediment samples were obtained from a mafic pro-glacial moraine and lakeshore in the Three Sisters volcanic complex [9] in central Oregon (44.156°N, -121.78°E; Fig 1). Fluid flow in the proglacial environment is dominated by seasonal ice/snow melt.

VNIR spectra of the bulk samples are dominated by alteration products (Fig. 2), with broad iron absorptions between 0.9-1.0  $\mu\text{m}$  that may be consistent with an iron oxide like ferrihydrite, 1.9  $\mu\text{m}$  bands that persist after heating that are most likely due to water in hydrated minerals and/or nanophase materials, and shallow bands near 2.20  $\mu\text{m}$  are consistent with an aluminosilicate (allophane, Al-smectites, etc.). However, 1.33 and 2.07  $\mu\text{m}$  bands are not consistent with any known phases and require further analysis.

Mid-IR spectral models of bulk samples (Fig. 3) are a mixture of primary minerals (plagioclase and minor pyroxene) and alteration products. The models include a major glass component, but as glass is unlikely, we hypothesize that this is the closest match in our library to a poorly crystalline alteration mineral, most likely an aluminosilicate like allophane [10].

Preliminary XRD patterns of the samples (Fig. 4), dry-sieved to <90  $\mu\text{m}$ , show that the crystalline component is dominated by primary minerals, with plagioclase with minor pyroxene and olivine peaks, but the two broad reflections at low angles indicate poorly crystalline phases. The broad maximum near  $\sim 14^\circ 2\theta$  is consistent with a poorly crystalline phyllosilicate. A smaller hump near  $\sim 3.4^\circ 2\theta$  might be indicative of a poorly crystalline silicate, like allophane.

The prevalence of alteration products in the VNIR spectra compared to the prevalence of crystalline primary phases in XRD suggests that the alteration phases are poorly crystalline, which is supported by the identification of amorphous silicate in our mid-IR models. Thus, these analyses support our general hypothesis

that sub-aerial weathering by snow/ice melt produces mainly poorly crystalline alteration phases.

**Cold climates on early Mars?** On Mars, poorly crystalline alteration phases have been detected as a major component of Noachian deposits sampled by landed missions. Models of MER Mini-TES mid-IR spectra of altered Clovis and Watchtower class rocks in Gusev Crater include up to 50% of an unknown poorly crystalline component [11]. Furthermore, nearly every unit sampled for CheMin XRD analysis by Mars Science Laboratory at Gale Crater contains a significant poorly crystalline component of variable composition [12,13]. We hypothesize that these poorly crystalline phases could be the result of weathering by ice/snow melt, perhaps providing some limited geochemical support for sustained cold climates on early Mars.

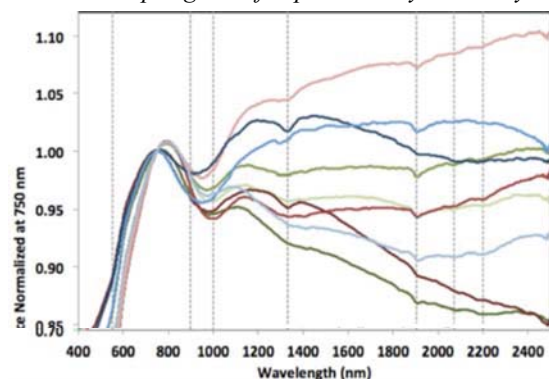
**A major unknown – subglacial weathering:** A major limitation of our ability to confirm or refute a dominantly cold climate on early Mars is that it is unknown what alteration minerals can be produced in the subglacial environment. On Earth, glacial weathering has been addressed exclusively through analysis of glacial outwash fluid chemistry. While these analyses have shown that wet glacial environments promote significant weathering [15], the mineralogy produced

is poorly understood [16], and therefore currently cannot be used to evaluate a glacial origin for alteration minerals on Mars. Glacial flour in distal lakes on Earth contains clay minerals that could be glacially sourced [17], suggesting that glaciers could have been a source of alteration minerals in lacustrine deposits on Mars. However, this has not been confirmed in the glacial environment on Earth. To rectify this knowledge gap, we are currently planning extensive field campaigns to sample glacial weathering products.

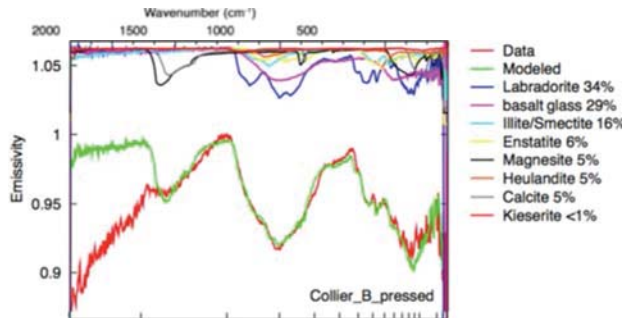
**References:** [1] Retallack et al (1999) *GSA Sp. Pap.* 344, 1-192. [2] Sheldon & Tabor (2009) *Earth Sci Rev* 95, 1-52. [3] Bourman (1993) *Aus J Earth Sci* 40, 387-401. [4] Horgan et al. (2014) 8<sup>th</sup> Mars, #1276. [5] Carter et al. (2015) *Icarus* 248, 373-382. [6] Ziegler et al (2003) *Chem Geo* 202, 461-478. [7] Arnalds (2004) *Catena* 56, 3-20. [8] Tsai et al. (2010) *Geoderma* 156, 48-59. [9] Hildreth et al (2012) USGS SIM 3186. [10] Rampe et al (2012) *Geology* 40, 995-998. [11] Ruff et al (2006) *JGR* 111, doi:10.1029/2006 JE002747. [12] Blake et al (2013) *Science* 341, doi:10.1126/science.1239505. [14] Vaniman et al. (2014) *Science* 343, 10.1126/science.1243480. [15] Anderson (2007), *An Rev Earth Planet Sci*, 35, 375-399. [16] Carrivick & Tweed, (2013) *Quat Sci Rev*, 78, 34-52. [17] Menking (1997) *GSA SP* 317, 25-36.



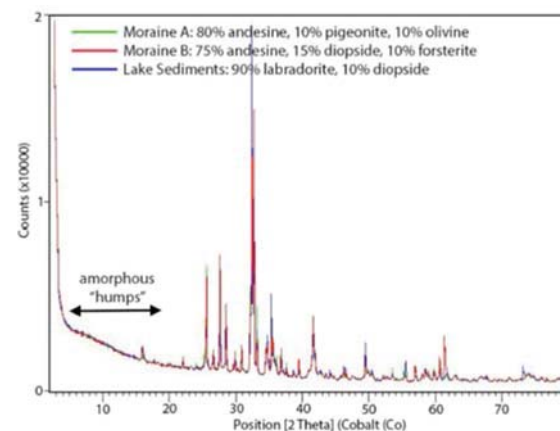
**Figure 1:** Collier Glacier pro-glacial moraine. Stars indicate sampling sites for preliminary lab analysis.



**Figure 2:** VNIR spectra of bulk proglacial samples, lines indicate absorptions most likely due to alteration.



**Figure 3:** Mid-IR spectra of bulk proglacial samples, with a poorly crystalline component modeled as glass.



**Figure 4:** XRD pattern of samples (sieved to <90  $\mu\text{m}$ ), showing primary minerals (sharp peaks) and poorly crystalline phases (humps at shorter wavelengths).